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<p>(21) International Application Number: PCT/US93/02099</p> <p>(22) International Filing Date: 8 March 1993 (08.03.93)</p> <p>(30) Priority data: 07/668,041 14 April 1992 (14.04.92) US</p> <p>(71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).</p> <p>(72) Inventors: SIEDLE, Allen, R.; LAMANNA, William, M.; Post Office Box 33427, Saint Paul, MN 55133-3427 (US).</p> <p>(74) Agents: PETERS, Carolyn, V. et al.; Office of Intellectual Property Counsel, Minnesota Mining and Manufacturing Company, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).</p>		<p>(81) Designated States: AT, AU, BB, BG, BR, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG).</p> <p>Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</p> <p>(88) Date of publication of the international search report: 20 January 1994 (20.01.94)</p>	
<p>(54) Title: TRIS(PENTAFLUOROPHENYL)BORANE COMPLEXES AND CATALYSTS DERIVED THEREFROM</p> <p>(57) Abstract</p> <p>Tris(pentafluorophenyl)borane complexes having the general formula $(C_6F_5)_3B(YXH)^q$ wherein X is oxygen, or sulfur; q is 1 to 3; Y is a hydrogen atom, R^1, $(R^2)_3Si$, or $(R^3)_2C=N-$; R^1 is a hydrocarbyl group containing 1 to 500 carbon atoms, and may contain a divalent oxygen and further may be a fluorine-containing hydrocarbyl group; R^2 is independently a linear or branched alkyl group containing 1 to 25 carbon atoms, or a phenyl group, further R^2 may contain a $SiO-$ group; and R^3 is independently a hydrocarbyl group containing 1 to 25 carbon atoms, R^3 may be a hydrogen atom provided both R^3 groups selected are not hydrogen atoms; and to complexes containing the borane complexes with an organometallic compound, either as a neutral compound or as an acidic salt that are useful as catalysts for polymerization and copolymerization of olefins and to polymeric products prepared using these catalysts.</p>			

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A. CLASSIFICATION OF SUBJECT MATTER		
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According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) IPC 5 C08F C07F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 426 637 (FINA TECHNOLOGY, INC) 8 May 1991 see page 4, line 27 - page 5, line 25 ---	11
A	DE,A,12 94 378 (KULZER & CO GMBH) 8 May 1969 see the whole document ---	1-3
A	EP,A,0 443 739 (AIR PRODUCTS AND CHEMICALS) 28 August 1991 see the whole document ---	1
A	EP,A,0 427 697 (FINA TECHNOLOGY, INC) 15 May 1991 see claims 1,17 see example 2 ---	11-22 -/-
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3	Date of the actual completion of the international search 3 December 1993	Date of mailing of the international search report 17.12.93
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016		Authorized officer Fischer, B

INTERNATIONAL SEARCH REPORT

Int'l Application No
PCT/US 93/02099

C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Description of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO,A,93 12151 (EXXON CHEMICALS PATENTS INC) 24 June 1993 see examples 3-6,8-12 ---	29
X	WO,A,91 04257 (EXXON CHEMICAL PATENTS INC) 4 April 1991 see examples 35-37 see examples 43,44,57 see example 36 -----	29
X		31

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INTERNATIONAL SEARCH REPORT

PCT/US93/02099

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(1).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See PCT/ISA/206 mailed on 27.08.1993

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- The additional search fees were accompanied by the applicant's protest.
 No protest accompanied the payment of additional search fees.

Information on patent family members

PCT/US 93/02099

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
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		US-A-	5096867	17-03-92

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TRIS(PENTAFLUOROPHENYL)BORANE COMPLEXES AND
CATALYSTS DERIVED THEREFROM

Field of the Invention

- 5 This invention relates to complex compounds of tris(pentafluorophenyl)borane and to mixtures containing the borane complexes and an organometallic complex that are useful as catalysts for polymerization
10 and copolymerization of olefins and to polymeric products prepared using these catalysts.

Background of the Invention

Use of soluble Ziegler-Natta type catalyst
15 systems in the polymerization of olefins, in particular polymerization of ethylene to polyethylene is known in the art. In general, traditional Ziegler-Natta type systems comprise a transition metal halide activated to form a catalyst species by reaction with
20 a metal alkyl cocatalyst, particularly aluminum alkyl cocatalysts. However, aluminum alkyl cocatalysts are often used in large excess, see U.S. Patent No. 4,404,344. This is disadvantageous because the aluminum compounds must be removed from the resultant
25 polymers. These traditional Ziegler-Natta catalysts often contain a variety of different active sites, each of which has its own rate of initiation, propagation, and termination. As a consequence of this non-uniformity of active sites, the linear
30 polyethylene has a broad molecular weight distribution. See for example, *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1982; Vol. 3, Chapter 22.5, p 475;
35 *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*; Kaminsky, W. and Sinn, H., Eds.; Springer-Verlag: New York, 1988, and *Transition Metal Catalyzed Polymerizations: Alkenes and Dienes*;

Quirk, R.P., Ed.; Harwood: New York 1983.

Recently, catalysts have been reported that rely on boron rather than on aluminum-containing compounds. Boron-based catalysts, in contrast, to the aluminum-based catalysts are often stoichiometric in boron. That is, they contain one mole of boron-containing component per mole of transition metal. Furthermore, it is usually unnecessary to remove the small amount of boron from the polymer, unlike the aluminum-based catalysts, mentioned above.

Tris(pentafluorophenyl)borane ($C_6F_5)_3B$ forms 1:1 complexes with Lewis bases such as ether, amines, and phosphines. The compound is hygroscopic and, presumably forms a monohydrate but neither the composition, that is stoichiometry of this hydrate nor its properties have been disclosed. No uses for these donor-acceptor complexes have been taught, see Massey et al. *J. Organomet. Chem.* 1964, 2, 245. Hygroscopic ($C_6F_5)_3B\text{-Et}_2O$ was reported by Pohlman et al. *Z. Nat.* 1965, 20b, 5.

Hlatky et al. *J. Am. Chem. Soc.* 1989, 111, 2728 described zwitterionic catalysts such as $(Me_2Cp)_2Zr[(m-C_6H_4)BPh_3]$. EPO 0 277 004 describes catalysts prepared by reacting $(Me_2Cp)_2ZrMe_2$ with $B_9C_2H_{13}$, $[Bu_3NH][(B_9C_2H_{11})_2Co]$ or $[Bu_3NH][B_9C_2H_{11}]$.

Similarly, EPO 0 418044 describes monocyclopentadienyl complex catalysts containing a non-coordinating, compatible anion such as $(C_6F_5)_4B^-$. More recently, homogeneous catalysts exemplified by $[Cp_2ZrMe][MeB(C_6F_5)_3]$ have been synthesized from the reaction of Cp_2ZrMe_2 and $(C_6F_5)_3B$ see X. Yang et al. *J. Am. Chem. Soc.* 1991, 113, 3623.

Furthermore, the above described catalysts are sparingly soluble in toluene. The catalysts are even less soluble in normally liquid α -olefins such as 1-hexene or in mixtures of such olefins and non-reactive solvents, such as hexane, toluene or xylene. These

- catalysts generally separate as oils from toluene or toluene-hexane mixtures. Even though catalysis still proceeds, phase separation is undesirable for several reasons, for example contact between soluble. When
- 5 the catalyst is incompletely soluble, catalyzed polymerization typically takes place at different rates either in solution or at the solid-liquid interface, thus tending to lead to a broad distribution of polymer molecular weights.
- 10 Furthermore, catalyst:monomer ratio in solution is generally difficult to control when the catalyst is only partially soluble.

It is further known that a soluble or molecularly dispersed catalyst typically permits more ready access

15 of the substrate to the active sites. As a result, more efficient use of the catalyst is possible. It is also recognized that the molecular weight of a polymer is proportional to the concentration of monomer in the reaction mixture in which it is synthesized.

20 Generally, high molecular weight is desirable in applications such as glues and adhesives, as well as in the construction of rigid objects such as gaskets, insulators and packaging materials.

Catalytic polymerization of lower olefins, in

25 particular ethylene and propylene is relatively easy. On the other hand polymerization of longer chain α -olefins tends to be slower and the products are often oligomers rather than high polymers, see Skupinska Chem. Rev. 1991, 91, 635. Heterogeneous catalysts

30 such as $TiCl_3/AlEt_2$, which produce higher molecular weight polymers from long-chain α -olefins, lead to a broad range of molecular weights (high polydispersity index).

Summary of the Invention

Briefly, in one aspect of the present invention catalyst precursor complexes are provided comprising tris(pentafluorophenyl)borane, $(C_6F_5)_3B$ and at least one complexing compound such as water, alcohols, mercaptans, silanols, and oximes. These neutral complexes may be converted to acidic salts of their conjugate bases by reaction with amines. The neutral complexes or acidic salts are reacted with Periodic Table Group IVB organometallic compounds to form catalytically active compounds (hereinafter also referred to as catalysts) useful for polymerization of olefin monomers. Advantageously, the catalysts of the present invention are soluble in olefins to the extent of 1×10^{-3} molar (M) or greater. Catalysts that can function in undiluted monomer, as distinguished from monomer dissolved in inert diluent, are desirable because the catalysts and monomers tend to produce products having higher molecular weight.

Additionally, because only low levels of the catalysts are used, removal of catalyst or its components from the final, product polymer is generally not required.

Catalysts of the present invention may be used to prepare polyolefins from olefinically unsaturated monomers having 2 to 30, preferably 5 to 10 carbon atoms. The resulting polymers have a weight average molecular weight of 100,000 to 5,000,000, preferably 500,000 to 3,500,000 and have a polydispersity (PD) of molecular weights ≤ 3.5 , preferably 1.5 to 3.

Polymers prepared from long chain α -olefins having high molecular weight and low polydispersibility are not previously described.

Suitable olefinically unsaturated monomers that may be polymerized using the catalysts of the present invention include, but are not limited to, linear- and branched α -olefins, cyclic olefins, olefins containing an aromatic group such as phenyl, olefins

containing silicon and boron, and diolefins. Mixtures of these monomers, as well as mixtures containing olefins and diolefins may be copolymerized. Preferred unsaturated monomers include linear α -olefins having

5 the general formula C_nH_{2n} , where n is 5 to 10.

A feature of the present invention is the incorporation of anions of the type $YX-B(C_6F_5)_2$ into novel complex salts of Group IVB transition metals (titanium, zirconium, and hafnium), to produce highly active catalysts capable of polymerizing longer chain poly- α -olefins to yield products having very high molecular weights and a narrow polydispersity index. Furthermore, preparation of these salts are described, and such salts can either contain or are essentially free of Lewis bases. An additional feature of this invention is the incorporation of flat carbocyclic ligands into these novel complex salts, to produce olefin polymers of exceptionally high molecular weight. Thus, as shown below using

20 $[(\text{ligand}), \text{ZrMe}] [(\text{C}_6\text{F}_5)_2\text{BOC}_2\text{H}_2]$ as the catalyst and 1-hexane as the monomer, polymer molecular weight increases as the ligand is changed in the order of cyclopentadienyl < indenyl << fluorenyl. The fluorenyl ligand is therefore particularly useful when

25 high molecular weight, rubbery polyolefins are desired.

In this application:

"Cp" means a carbocyclic ligand, such as

30 cyclopentadienyl, indenyl or fluorenyl;

"Me" means a methyl group;

"Et" means an ethyl group;

"Bu" means a butyl group;

"Ph" means a phenyl group;

35 "hydrocarbyl" is used in its usual sense to mean a group containing hydrogen and carbon atoms, such as alkyl, alkényl, aryl, cycloalkyl, cycloalkenyl,

alkaryl, arylalkyl, and the like; and

"Group IVA" and "Group IVB" are the Periodic Table CAS version designations.

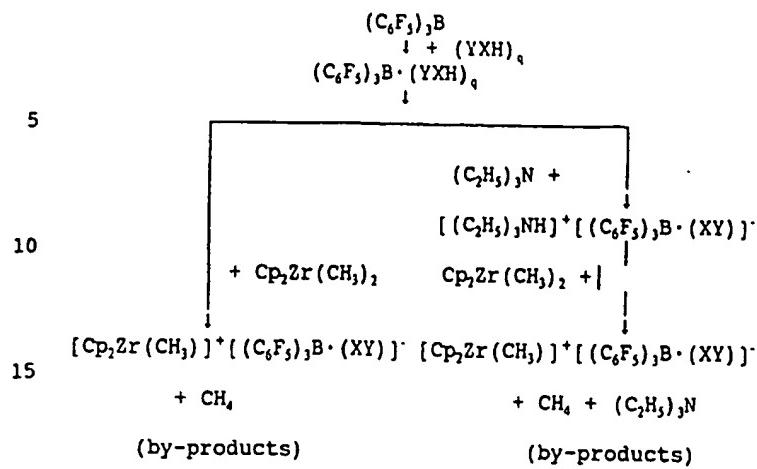
5 Detailed Description of the Preferred Embodiment

The compound $(C_6F_5)_3B$, tris(pentafluorophenyl)borane (also referred to as tris(pentafluorophenyl)boron), forms Lewis base complexes with a wide variety of alcohols, mercaptans, silanols, and oximes. These borane complexes are catalyst precursors that when combined with Group IVB organometallic compounds produce catalysts useful for polymerization of olefins, such that the polymers have high molecular weights and low polydispersities, that is a narrow molecular weight distribution.

Lewis base complexes of $(C_6F_5)_3B$ bearing at least one acidic hydrogen atom on the boron-bound heteroatom are useful for preparing catalysts. These compounds can be represented by the general formula: $(C_6F_5)_3B \cdot (YXH)^q$ wherein X, Y and q are as described below and the valence of X is completed with hydrogen atoms where necessary to provide a neutral compound.

The following reaction scheme illustrates how neutral Lewis base complexes of tris(pentafluorophenyl)borane and corresponding acidic salts may be prepared. For illustration purposes, the reaction scheme depicts $(C_2H_5)_3N$ as a reactant to produce acidic salts. Without intending to be bound by theory, reaction scheme further illustrates how the neutral Lewis base complexes of tris(pentafluorophenyl)borane and the corresponding acidic salts are believed to react with Group IVB organometallic complexes to produce the catalytically active salts of this invention.

7



20 wherein Y, X, and q are as defined below

The neutral borane complexes have the general formula

25 $(\text{C}_6\text{F}_5)_3\text{B} \cdot (\text{YXH})_q$
 wherein X is oxygen, or sulfur;
 q is 1 to 3, preferably q is 1;
 Y is a hydrogen atom, R^1- , $(\text{R}^2)_3\text{-Si}$, or $(\text{R}^3)_2\text{C}=\text{N}-$;
 R^1 is a hydrocarbyl group containing 1 to 500,
 30 preferably 1 to 100 carbon atoms, and may contain
 a divalent oxygen and further may be a halogen-
 containing hydrocarbyl group, for example the R^1
 group can be $\text{CH}_3\text{OC}_2\text{H}_4-$, t-butylcyclohexyl,
 isopropyl, allyl, benzyl, methyl, ethyl, $\text{C}_{11}\text{H}_{17}$,
 35 oligomeric poly- α -olefins (containing 2 to 100
 monomeric units), or $\text{CF}_3\text{CF}_2(\text{C}_2\text{F}_5)_n\text{C}_2\text{H}_4-$, where n has
 an average value of 3.5;
 R^2 is independently a linear or branched alkyl group.
 containing 1 to 25 carbon atoms, or a phenyl
 40 group, further R^2 may contain a SiO-group, for
 example $(\text{R}^2)_2$, may be $(t\text{-C}_4\text{H}_9)(\text{CH}_3)_2-$ or $((\text{CH}_3)_2\text{SiO})_2-$;
 and
 R^3 is independently a hydrocarbyl group containing 1 to

25 carbon atoms, further R¹ may be a hydrogen atom provided both R¹ groups selected are not hydrogen atoms, for example when X is oxygen, (R¹)₂C=NOH forms oximes, a compound (either cis or trans) containing the oxime group =C=NOH, and is a condensation product of aldehydes or ketones with hydroxylamine.

- Tris(pentafluorophenyl)borane tends to form
- 10 complexes with alcohols having the general formula R'OH. For example, treatment of (C₆F₅)₃B with methanol liquid or vapor produces the bis(solvate) (C₆F₅)₃B·2MeOH. No significant amount of methanol can be removed by pumping at room temperature. This compound can be
- 15 converted to (C₆F₅)₃B·MeOH by treatment with one equivalent of (C₆F₅)₃B. The 1:1 complex (C₆F₅)₃B·MeOH may also be prepared by reacting (C₆F₅)₃B with one equivalent of methanol. Isopropanol forms a bis(solvate) as well but one equivalent of alcohol is removed under vacuum
- 20 at room temperature.

Tris(pentafluorophenyl)boron complexes of less volatile alcohols can be prepared by combining one equivalent each of an alcohol and (C₆F₅)₃B in a suitable, nonreactive solvent such as chloroform or toluene,

25 followed by evaporation of the solvent. Suitable alcohols contain a wide variety of aliphatic or aromatic groups including but not limited to linear (stearyl alcohol), cyclic (t-butylcyclohexanol), branched (isopropanol), unsaturated (allyl alcohol),

30 aromatic (benzyl alcohol), optically active (menthol), oxygen-substituted (MeOC₂H₅OH), oligomeric (poly-1-hexene alcohol), and halogen-substituted [CF₃CF₂(C₂F₅)_nC₂H₅OH], where n has an average value of 3.5.

Suitable alcohols generally have pKa values

35 between -2 and -4. For example, 2,2,2-trifluoroethanol and phenol do not form isolable complexes. Formation of a stable complex is readily ascertained by boron

nuclear magnetic resonance (^{11}B NMR) spectroscopy. The $(C_6F_5)_3B$ complexes of this invention have chemical shifts between -5 and + 15 ppm (relative to external $BF_3 \cdot OEt_2$) compared with +60 ppm for the swung material $(C_6F_5)_3B$.

- 5 Other specific examples of $(YXH)_q$ (when q is 1) include silanols ($(R^2)SiOH$), mercaptans ($R'SH$), and oximes ($(R_2)C=NOH$). Examples of silanols include but are not limited to $(t-C_4H_9)Me_2SiOH$ and $(Me_2SiO)_2SiOH$. Higher mercaptans having low vapor pressures are
10 preferred in catalyst applications such that the polymers produced do not have an objectionable odor. An example of a mercaptan useful in the present invention is octadecyl mercaptan. Examples of oximes include acetone oxime and cyclohexanone oxime.
- 15 Of the class of compounds of the type $(C_6F_5)_3B-(YXH)_q$, when Y is hydrogen, X is oxygen, and q is 1 or 3, the complex with water is a special case. Exposure of anhydrous $(C_6F_5)_3B$ to water vapor, produces $(C_6F_5)_3B \cdot 3H_2O$, a white, stable solid. No intermediate
20 hydrate was detected by infrared spectroscopic analysis. The water content was demonstrated by a single crystal X-ray structure determination. Formation of a trihydrate was unexpected because all other previously known $(C_6F_5)_3B$ complexes with Lewis
25 bases have a 1:1 stoichiometry. Vacuum sublimation of the trihydrate produced a mixture of the monohydrate and $(C_6F_5)_3B$. The pure monohydrate, $(C_6F_5)_3B \cdot H_2O$, however may be obtained by combining in organic solvents, such as toluene or chloroform, one equivalent of $(C_6F_5)_3B \cdot 3H_2O$
30 with two equivalents of $(C_6F_5)_3B$ followed by evaporation of the solvent. This conproportionation reaction is a convenient way of synthesizing the monohydrate as needed. Unlike $(C_6F_5)_3B \cdot 3H_2O$, $(C_6F_5)_3B \cdot H_2O$ is unstable and slowly decomposes, either in solution or in the solid
35 state, to $(C_6F_5)_2BOH$ and C_6F_5H . The monohydrate may also be prepared by combining one mole each of water and

$(C_6F_5)_3B$.

The heteroatom-bound protons in Lewis base complexes of $(C_6F_5)_3B$, such as $(C_6F_5)_3B \cdot R'OH$ and $(C_6F_5)_3B \cdot R'SH$ are acidic and can be removed by treatment 5 with bases such as primary, secondary, or tertiary amines. For example, reaction of $(C_2H_5)_3N$ with $(C_6F_5)_3B \cdot 3H_2O$ or $(C_6F_5)_3B \cdot 2CH_3OH$ produces the acidic salts $[C_2H_5]NH^+[(C_6F_5)_3BOH]^-$ and $[Et_3NH]^+[(C_6F_5)_3BOCH_3]^-$ respectively. Preferred bases are triethylamine, 10 tributylamine and N,N-dimethylaniline.

Catalysts useful for polymerization of olefinic hydrocarbons may be prepared using the precursor borane complexes and hydrocarbylcyclopentadienyl metal complexes having the general formula:

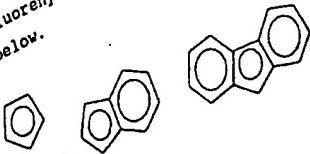
15 $(Cp)_pM(R')_{4-p}$ (II)

wherein M is titanium, zirconium or hafnium;

p is 1 or 2

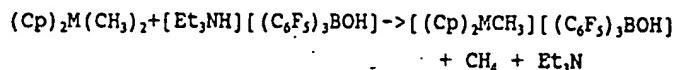
20 Cp is a cyclopentadienyl ligand, wherein each carbon atom in the ring may be, independently, substituted with a radical selected from the group consisting of hydrocarbyl radicals, hydrocarbyl-substituted metalloid radicals wherein the metalloid is selected from Group IVA of the Periodic Table of the elements wherein the hydrocarbyl and substituted-hydrocarbyl radicals contain 1 to 25 20 carbon atoms and can include straight and branched alkyl groups, cyclic hydrocarbon groups, alkyl-substituted cyclic hydrocarbon groups, aromatic groups or alkyl-substituted aromatic groups; one or two pairs of adjacent hydrogen atoms of the cyclopentadienyl ligand may be substituted with one or two $-(CH_2)-$ groups to form indenyl or fluorenyl radicals, respectively; further, compounds in which one 30 or two methylene rings having the general formula $(CH_2)_n$ wherein n is 3 to 6 may be 35

11
5 substituted for two adjacent hydrogen groups
in the cyclopentadienyl ligand; further, when
p is 2, the cyclopentadienyl ligands may be
combined into one bidentate ligand molecule by
10 connecting the cyclopentadienyl ligands by
an organic or organometalloid group containing
1 to 20 carbon atoms and may be a straight or
branched alkyl group, a cyclic hydrocarbyl or
15 aromatic group, an alkyl-substituted cyclohydrocarbyl group, an
aromatic group (e.g., benzyl), or an alkyl-substituted alkyl
group on the metalloid contains from 1 to 20
20 Group IVA elements wherein each hydrocarbyl
carbon atoms.
25 Suitable examples of Cp include but are not
limited to cyclopentadienyl, indenyl, fluorenyl,
bis(octahydrofluorenyl), 1,2-bis(1-indenyl)ethane, 1,2-
bis(tetrahydroindenyl)ethane, 1,3-bis(9'-
isopropyl(cyclopentadienyl)-1-fluorenyl) and 1,3-bis(9'-
fluorenyl)propane. Chiral metallocenes are also
suitable and useful when a stereoregular polymer is
desired. General structures of cyclopentadienyl,
indenyl and fluorenyl ligands, respectively are
30 represented below.



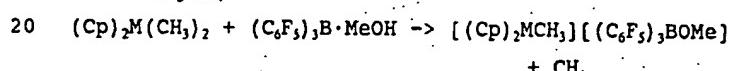
While not intending to be bound by theory, the organometallic complex, $(Cp)_2M(R^4)_2$, is believed to react with acid salts of the anions, such as $(C_6F_5)_3B \cdot OR^1$, $(C_6F_5)_3B \cdot OH$, $(C_6F_5)_3B \cdot SR^1$, $(C_6F_5)_3B \cdot OSi(R^2)_3$, or $(C_6F_5)_3B \cdot ON=C(R^3)_2$ (containing at least one acid proton in the cationic portion of the salt) to form byproducts and catalytically active salts containing $(Cp)_2M(R_3)_2$. For example, this can be illustrated by the following reaction with $[Et_3NH][(C_6F_5)_3BOH]$.

10



(Reaction Scheme I)

15 Alternatively, the need for an acidic salt can be bypassed in the direct reaction of the metal complexes with neutral complexes of tris(pentafluorophenyl)borane with water, alcohols, mercaptans, silanols or oximes. For example,



(Reaction Scheme II)

Materials prepared by either route can be used as catalysts for the polymerization of olefins.

25 Importantly, catalysts prepared according to Reaction Scheme II can be obtained free of extraneous Lewis base byproduct such as triethylamine (obtained in Scheme I).

Materials described in this invention are useful for polymerization of olefins such as ethylene and propylene and in particular higher olefins, for example, 1-hexene or 1-octene. Polyolefins having high weight average molecular weights may be prepared by treating undiluted olefins with a catalytically effective amount of a catalyst of the present invention. Optionally, the polyolefins may be diluted with an inert diluent, such as toluene or hexane.

Catalysts of the present invention may be used to

- 5 prepare polyolefins from olefinically unsaturated monomers having from 2 to 30, preferably 5 to 10 carbon atoms. The resulting polymers have a weight average molecular weight of 100,000 to 5,000,000, preferably 500,000 to 3,500,000 and have a polydispersity (PD) of molecular weights \leq 3.5, preferably 1.5 to 3. Polymers prepared from longer chain olefins, for example, $C_6H_{2n}(n \geq 5)$ olefins having high molecular weight and low polydispersity have not been previously described.
- 10 Olefinically unsaturated monomers that may be polymerized using the catalysts of the present invention include, but are not limited to, linear- and branched α -olefins, cyclic olefins, olefins containing an aromatic group such as phenyl, olefins containing 15 silicon and boron, and diolefins. Mixtures of these of monomers, as well as mixtures containing olefins and diolefins may be copolymerized.

Tabl 1

Polyhexanes Obtained
with
5 Different Metanocenium Ion Catalysts^(a)

	Initiator	Degree of Polymerization ^(b)	% Conversion
10	Cp ₂ ZrMe ⁺	99	100
	(indenyl) ₂ ZrMe ⁺	200	70
	(Me ₃ Cp) ₂ ZrMe ⁺	83	100
	[(Me ₃ Si) ₂ Cp] ₂ HfMe ⁺	66	51
	(Me ₃ Cp) ₂ HfMe ⁺	118	100
	(Me ₃ SiCp) ₂ HfMe ⁺	60	98
15	(Me ₃ SiCp) ₂ HfMe ^{+(c)}	56	90
	Cp ₂ HfMe ⁺	429	100
	Cp ₂ HfMe ^{+(d)}	506	100
	(indenyl) ₂ HfMe ⁺	1025	100
	(Me ₃ SiCH ₂ Cp) ₂ ZrMe ⁺	19	4
	(n-C ₄ H ₇ Cp) ₂ HfMe ⁺	23	94
20	(Me ₃ SiCp) ₂ ZrMe ⁺	10	55
	[Me ₃ Si(C ₂ H ₅) ₂]ZrMe ⁺	4	<1
	(PhCH ₂ SiMe ₂ Cp) ₂ ZrMe ⁺	7	88
	(fluorenyl) ₂ ZrMe ⁺	4800	69
	[(indenyl) ₂ C ₂ H ₅] ₂ ZrMe ⁺	156	87
	[(indenyl) ₂ C ₂ H ₅] ₂ HfMe ⁺	271	78

(a) Conditions: C₁₀H₁₇O·B(C₆F₅)₃ salts in 0.5 mL toluene-1-hexene, monomer:catalyst 6400:1 at 0°C

(b) determined by ¹H NMR analysis and refers to the average number of monomer units in the polymer chain

(c) anion is C₁₀H₁₇S·B(C₆F₅)₃

(d) anion is conjugate base of polyhexene alcohol·B(C₆F₅)₃

35 Ring substitution on the Cp ligand in the catalysts of the present invention can lead to reduced polymer molecular weight and activity. This is illustrated in Table 1. Reduction of polymer molecular weight is generally undesirable in many applications since it is associated with loss of polymer cohesive strength. For example, decreases in molecular weight

associated with the Me₂Si group has not been described before. It is surprising because catalysts prepared from (Me₂SiCp)₂ZrMe₂ and methyl aluminoxane tend to produce higher molecular weight polyhexane than does 5 unsubstituted Cp₂ZrMe₂.

An advantage of the present invention is the permissible introduction of solubilizing groups that enhance solubility of catalyst salts in the olefinic monomer or solution of monomer and solvent into the 10 anion rather than the cation that contains the active catalytic site. The solubilizing groups are spatially removed from the active site, and therefore do not interfere with polymerization and thus produce polymers of high molecular weight. For example, the catalyst 15 [(indenyl)₂ZrMe]₂[(C₆F₅)₂B·OC₁₈H₃₇], in which the anion contains the solubilizing octadecyl group that was introduced via of the alcohol Complex (C₆F₅)₂B·C₁₈H₃₇OH, is soluble to the extent of about 10³ M in 80:1 (v/v) 1-hexene-toluene. In an other example, polyhexene 20 alcohol having an average degree of polymerization of 5.9 and bearing a terminal CH₂OH group, yielded a solution as concentrated as 10³ M in 40:1 hexene-hexane. For example, the structure of the solubilizing group can be varied so as to produce good catalyst 25 solubility in a monomer of choice by suitably modifying the structure of R'OH in (C₆F₅)₂B·R'OH. As illustrated in the examples below, the anions of the present invention provide catalysts that produce higher molecular weight polyolefins than superficially related catalysts, even 30 at equivalent monomer: catalyst ratios.

Although (indenyl)₂ZrMe, organometallic compounds are reportedly useful in the preparation of catalysts, there appears to be no correlation between the structure of the ligand(s) in the organometallic 35 portion of the catalyst and the molecular weights of polymers of higher olefins (C5 and greater) produced with such catalysts. As a result, it is not readily

apparent which organometallic compounds may be used to prepare high molecular weight polymers. For example, the soluble, homogeneous olefin polymerization catalysts described by U.S. Patent No. 4,404,344 5 (Kaminsky et al.) when used to prepare poly(hexene), produces oligomers having molecular weights less than 50,000.

Structurally, flat cyclopentadienyl ligands, when incorporated into these complex salts, produce polymers 10 of high molecular weight. As shown in Table 1 above, using [(ligand)₂ZrMe]_n[$(C_6F_5)_2B\cdot OC_{11}H_{17}$] as the catalyst and 1-hexene as the monomer, the degree of polymerization in the product polymer increased from 99 to 200 to 4800 15 as the ligand was changed in the order from cyclopentadienyl to indenyl to fluorenyl, respectively. The fluorenyl ligand is particularly useful when high molecular weight, rubbery polyolefins are desired.

Objects and advantages of this invention are further illustrated by the following examples, but the 20 particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit the invention.

25

Examples

All compounds were characterized by at least one of infrared (IR) and nuclear magnetic resonance (NMR) spectroscopies. NMR analysis included ¹H, ¹³C, and ¹⁹F. Number average molecular weight (M_n) and weight 30 average molecular weight (M_w) for polymers having M_w less than 10^6 were determined by gel permeation chromatography (GPC) using polystyrene standards or by NMR analysis as is known to those skilled in this art. Polydispersity (PD) refers to the weight-average 35 molecular weight divided by the number average molecular weight, that is, M_w/M_n .

Materials whose weight average molecular weight

exceeded 10^6 were characterized by low angle laser light scattering techniques as is known to those skilled in this art. All starting materials and solvents are commercially available or known in the literature, unless 5 otherwise stated or apparent. All commercially available materials and solvents are available from Aldrich Chemical Co., unless otherwise noted.

Preparation Example 1

10 Preparation of $(C_6F_5)_3B$

Tris(pentafluorophenyl)borane was prepared by the reaction of C_6F_5Li with BCl_3 in hexane at temperatures below $-50^\circ C$ according to the procedure described in Massey et al. *J. Organomet. Chem.* 1964, 2, 245.

15

Example 1

Preparation of $(C_6F_5)_3B \cdot 3H_2O$

A 0.87 gram quantity of $(C_6F_5)_3B$ was placed in one leg of a reactor consisting of an inverted U-tube, 20 closed at both ends and fitted with a stopcock and O-ring joint so that the apparatus could be connected to a vacuum line. Excess water was placed in the other leg. After the water had been frozen with a low temperature bath, the apparatus was evacuated. After 25 warming the reactor to room temperature, the borane reacted with water vapor to form the trihydrate. After water uptake was completed, excess water was pumped away to provide the air-stable product in quantitative yield.

30

Example 2

Preparation Of $(C_6F_5)_3B \cdot H_2O$

A mixture of 0.566 gram (1 mmol) $(C_6F_5)_3B \cdot 3H_2O$ as prepared in Example 1 and 1.024 grams (2 mmol) $(C_6F_5)_3B$ 35 in 10 mL dichloromethane was stirred for 15 minutes and then evaporated to dryness under vacuum. A quantitative yield of the product remained and was

stored under dry nitrogen.

Example 3

Preparation of $[Et_3NH]_2(C_6F_5)_2BOH$

- 5 A solution of 3.6 grams $(C_6F_5)_2B \cdot 3H_2O$ as prepared in Example 1 in 20 mL toluene was treated with 0.76 gram triethylamine in 3 mL of the same solvent. The reaction mixture was diluted with 50 mL hexane to precipitate 2.75 gram of crude product. Using Karl 10 Fisher analysis, the crude product was determined to be a hydrate and the % H_2O present was 0.66. The crude product was recrystallized by solution in a minimum amount of hot toluene, followed by cooling to -50°C. Filtration and vacuum drying yielded a material 15 containing 0. 15 % H_2O (by weight), corresponding to 5 mole per cent H_2O .

Example 4

Preparation of $(C_6F_5)_2B \cdot 2MeOH$

- 20 A solution of 0.34 gram of $(C_6F_5)_2B$ in 1.5 mL methanol was prepared under dry N_2 and evaporated to dryness to yield a clear viscous residue that crystallized under dynamic vacuum (vacuum pumping) overnight. The yield was 0.33 gram.

25 Example 5

Preparation of $[Ph_3PMe]_2(C_6F_5)_2BOMe$

- A solution of 0.39 gram (0.76 mmol) of $(C_6F_5)_2B$ in 1 mL methanol was treated with a slight excess (>5%) of methanolic sodium methoxide. Excess 30 methyltriphenylphosphonium bromide was then added to the solution. The solution was diluted to the cloud point with water and then refrigerated. White crystals were collected on a filter, washed with water and vacuum dried. The yield was 0.58 grams (93%).

Example 6

A similar reaction to Example 5 was used to prepare the triethylammonium salt but, under these conditions, partial hydrolysis of the anion to 5 $(C_6F_5)_3BOH^-$ occurred.

Example 7Preparation of $(C_6F_5)_3B \cdot C_{18}H_{37}OH$

A solution of 0.135 gram (0.5 mmol) of 1-octadecanol and 0.256 gram (0.5 mmol) of $(C_6F_5)_3B$ in 4 10 mL toluene was stirred for 30 minutes. The solution was then evaporated on a vacuum line. The remaining product was as a viscous oil, and the yield was approximately 0.37 gram. The $(C_6F_5)_3B$ complex was prepared and handled in an atmosphere of dry nitrogen.

15

Example 8Preparation of $(C_6F_5)_3B \cdot C_{18}H_{37}SH$

A solution of 0.143 gram (0.5 mmol) of 1-octadecyl mercaptan and 0.356 gram (0.5 mmol) of $(C_6F_5)_3B$ in 5 mL 20 dichloromethane was evaporated under high vacuum. The residual product was an oil weighing 0.36 gram.

Example 9Preparation Of $(C_6F_5)_3B \cdot C_3H_7OC_2H_5OH$

25 A solution of 0.059 gram (0.5 mmol) of 2-butoxyethanol, dried over 4A molecular sieves and 0.256 gram (0.5 mmol) of $(C_6F_5)_3B$ in 1 mL toluene was evaporated under high vacuum. The residual product was a viscous oil and the yield was approximately 0.24 30 gram.

Example 10Preparation Of $(C_6F_5)_3B \cdot cyclo-C_6H_{10}-NOH$

A solution of 0.056 gram (0.5 mmol) of 35 cyclohexanone oxime and 0.256 gram of $(C_6F_5)_3B$ in 2.5 mL dichloromethane was evaporated under high vacuum to leave 0.28 gram of product.

Example 11Preparation of $(C_6F_5)_3B \cdot (Me_2SiO)_2SiOH$

A solution of 0.312 gram (1 mmol) of tris(trimethylsiloxy)silanol (PCR, Inc., Gainesville, FL) and 0.512 gram (1 mmol) of $(C_6F_5)_3B$ in 1.5 mL toluene was stirred for 30 minutes and then evaporated under high vacuum. There remaining 0.8 gram of product was a white semi-solid.

10

Example 12

Fluorinated alcohol complex

Tris(pentafluorophenyl)borane (0.51 gram, 1 mmol) and 0.44 gram (1 mmol) of $CF_3CF_2(CF_2CF_2)_nCH_2CH_2OH$ (as prepared in U.S. Patent No. 4,219,681, Example 1 and such description is incorporated herein by reference) in which the average value of n was 3.5 were combined under dry nitrogen in 2 mL of $CF_2ClCFCl_2$. After stirring the solution for approximately 1 hour, the solvent was evaporated to leave a fluorinated alcohol complex as a greasy solid.

Example 13Polymerization using $(C_6F_5)_3B \cdot H_2O$

1. Preparation of $(C_3H_5)_2ZrMe_2$
25 $(C_3H_5)_2ZrMe_2$ was prepared by treatment of $(C_3H_5)_2ZrCl_2$ in diethyl ether with two equivalents of methylolithium as described in Samuel et al. *J. Am. Chem. Soc.* 1973, 9, 6263.
2. 1-Hexene (0.67 gram) was added under nitrogen to a
30 catalyst prepared by combining 0.05 mmole each of $(C_6F_5)_3B \cdot H_2O$ prepared according to Example 2 and $(C_3H_5)_2ZrMe_2$. After a few seconds, an exothermic reaction occurred and the mixture became thick. After approximately 50 minutes, any suspended catalyst was
35 removed by centrifugation. Unreacted monomer was then evaporated. NMR (1H) analysis showed that the resultant polymer had a number average molecular weight (M_n) of

400. The yield of polymer was 95%.

Example 14

Polymerization using $(M_2Cp)HfMe_2$,

- 5 1. Preparation of $(Me_2C_2)HfMe_2$,
 $(Me_2C_2)HfMe_2$, was prepared by reacting $(Me_2C_2)HfCl_2$,
with 3 equivalents of methyllithium as described in
Schock et al. J. Am. Chem. Soc. 1988, 110, 7701.
2. A reaction similar to that in the Example 13 was
10 carried out using $(Me_2C_2)HfMe_2$, instead of $(C_2H_5)_2ZrMe_2$.
The yield of polymer, with an Mn of 2200, was 90%.

Example 15

Polymerization using $[Et_2NH]_2(C_6F_5)_2BOH$

- 15 To 0.31 gram (0.5mmol) of $[Et_2NH]_2(C_6F_5)_2BOH$ (as
prepared in Example 3) suspended in 6 mL toluene was
added dropwise under dry nitrogen with stirring 0.13
gram (0.5 mmol) $(C_2H_5)_2ZrMe_2$, (as prepared in Example
13(1)) in 1 mL of the same solvent. Gas evolution
20 occurred. The resulting orange oil that separated was
removed by decantation, washed with toluene, then
hexane, and vacuum dried to give 0.31 gram of catalyst
as an orange foam.

This catalyst (0.01 gram) was added under dry
25 nitrogen to 0.67 gram of 1-hexene. After 3 days, the
reaction mixture was diluted with hexane and filtered
to remove any undissolved catalyst. Evaporation of the
hexane left 0.45 gram of polymer. Gel permeation
chromatography (GPC) revealed that the product had $M_w =$
30 $27,700$, $M_n = 9100$ and PD = 3.04.

Example 16

Soluble catalyst prepared using $(C_6F_5)_2B \cdot C_{18}H_{37}OH$

- A solution of 0.05 mmol $C_{18}H_{37}OH$ in 0.3 mL toluene
35 was added under dry N₂ to 0.05 mmol of $(C_6F_5)_2B$. Then,
0.05 mmol of $(C_2H_5)_2HfMe_2$, as prepared in Example 14 was
added to the solution. Approximately, one half of the

resulting catalyst solution was added with stirring to 13.4 gram dry, oxygen-free 1-hexene that had been cooled to 0°C, the monomer:catalyst ratio was 6400:1. The reaction mixture was essentially clear and
5 transparent, that is, no suspended solids were observed. After approximately 16 hours, the polymer product was removed from the reactor by dissolution in hot heptane. After the heptane had been stripped at 95°C using a water aspirator, 13.6 grams of polymer
10 remained having $M_w = 148,000$, $M_n = 55,500$ and PD = 2.67.

Examples 17(a) and 17(b)

Reactions similar to Example 16 were carried out using the boron complex prepared according to Example
15 16 and

(a) $(Me_3SiC_3H_4)_2HfMe_2$ was prepared by reacting Li[Me₃SiC₃H₄] and HfCl₄ in tetrahydrofuran followed by alkylation with methyllithium. The monomer:catalyst ratio was 6400:1. The resulting polymer had an M_n of
20 5040 as determined by NMR analysis; and
(b) $(n-C_8H_{17}C_3H_4)_2HfMe_2$ was prepared by reacting NaC₃H₅ in liquid ammonia with 1-C₈H₁₇Br to provide n-C₈H₁₇C₃H₄. This was then converted by reaction with n-C₈H₁₇Li and then HfCl₄ to provide $(n-C_8H_{17}C_3H_4)_2HfCl_2$.
25 Subsequent alkylation with methyllithium produced $(n-C_8H_{17}C_3H_4)_2HfMe_2$. The monomer:catalyst ratio was 3200. The resulting polymer had an M_n of 1932 as determined by NMR analysis.

30

Example 18

Polymerization using oligomeric (polyhexene) alcohol

A reaction like that in Example 16 was carried out using an oligomeric (polyhexene) alcohol. (average degree of polymerization 5.9) instead of octadecanol.
35 The oligomeric (polyhexene) alcohol was prepared according to the procedure described in Examples 1a and 1b of co-pending U.S. patent application, Serial No.

07/_____, filed April 9, 1992 (Attorney Docket No. 47866USA5A) and such description is incorporated herein by reference. The yield of polymer was essentially quantitative. GPC analysis showed the polymer had $M_w = 5$ 164,000, $M_n = 63,000$ and PD = 2.6.

Example 19

Comparative example using background art catalyst

Hexene was catalytically polymerized using
10 [(C₅H₅)₂HfMe][MeB(C₆F₅)₂], similar to the Zr analogue described in Yang et al. *J. Am. Chem. Soc.* 1991, 113, 3623.

Cp₂HfMe, and (C₆F₅)₂B (0.025 mmol each) were combined in 0.7 mL anhydrous toluene in a dry nitrogen atmosphere. Reaction occurred and a yellow oil separated. The yellow oil was dispersed by shaking and added to 13.4 grams of dry, oxygen-free 1-hexene at 0°C. Separation of a solid catalyst phase was observed. After approximately 48 hours, the resultant 15 polymer was removed from the reactor by dissolving it in hot cyclohexane. The polymer, after removing the solvents under water aspirator vacuum weighed 13.6 grams (some residual solvent was present). GPC analysis revealed that the polymer had $M_w = 20$ 48,000, $M_n = 25$ 13,500 and PD = 3.55. The molecular weight of the polymer was lower, and the polydispersity higher than that of the material produced under similar conditions in Example 16.

Example 20

Polymerization using (C₆F₅)₂B·C₁₈H₃₇SH

To a solution of 0.05 mmol of the 1-octadecyl mercaptan complex of (C₆F₅)₂B as prepared in Example 8 was added under nitrogen with stirring 0.024 gram (0.05 35 mmol) of (Me₂SiCp)₂HfMe, in 0.1 mL anhydrous toluene. This mixture was then added to 13.4 grams of dry, oxygen-free 1-hexene. After approximately 48 hours,

the polymer was dissolved in heptane, and then filtered through a pad of granular alumina. After evaporation of the solvent under reduced pressure, there remained 10.2 grams of polymer having an M_n of 4900 as determined by ^1H NMR.

Example 21

Polymerization using $(\text{C}_6\text{F}_5)_3\text{B}\cdot(\text{MeSiO})_2\text{SiOH}$

A toluene solution (0.3 mL) containing 0.025 mmol each $(\text{C}_6\text{F}_5)_3\text{B}\cdot(\text{MeSiO})_2\text{SiOH}$ and $(\text{indenyl})_2\text{HfMe}_2$ as prepared in Example 14 was added with stirring to 13.4 grams of dry, oxygen-free 1-hexene that had been cooled to 0°C. After approximately 16 hours at this temperature, the polymer weighed 23 grams. NMR analysis disclosed that the polymer contained 5 mole % 4-methyl-1-pentene. According to GPC analysis, the polymer had $M_w = 207,000$, $M_n = 62,000$ and PD 3.3. reactor was opened to air, a small amount of toluene was added and the resulting product scraped into a jar. After the volatiles were removed at 95°C/6.7 hPa (5 mm Hg), 11.3 grams of polymer remained. The polymer had an $M_w = 340,000$, $M_n = 145,000$ and PD = 2.34.

Example 22

Polymerization using $(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{cyclo-C}_6\text{H}_{10}=\text{NOH}$

A suspension in 0.85 mL toluene of a catalyst prepared from 0.025 mmole each of the $(\text{C}_6\text{F}_5)_3\text{B}\cdot$ cyclohexanone oxime complex as prepared in Example 10 and $(\text{indenyl})_2\text{HfMe}_2$ was added with stirring to 13.4 grams of cold (0°C) dry, oxygen-free 1-hexene. After approximately 16 hours, the organic phase was removed and evaporated to give 1.2 grams of polymer having M_n of 31,000 as determined by NMR analysis.

Example 23

Polymerization using $(C_6F_5)_3B \cdot BuOC_2H_4OH$

In 0.3 mL anhydrous toluene were combined 0.025 mmole each of the butoxyethanol complex as prepared in Example 9 and $(indenyl)_2HfMe_2$. Then 0.67 gram of 1-hexene was added. After approximately 16 hours, the reaction mixture was evaporated to give 0.44 gram (66%) of polymeric product having M_w of 18,000 as determined by NMR.

10

Example 24

Copolymerization of 1-hexene and 4-methyl-1-pentene

This example illustrates the preparation of a copolymer of two different olefins. A catalyst was prepared from 0.025 mmole each $(indenyl)_2HfMe_2$ and $(C_6F_5)_3B \cdot C_11H_9OH$ as prepared in Example 7 in 0.3 mL of dry, oxygen-free toluene. The catalyst was added with stirring to a mixture of 26.8 grams of dry, oxygen-free 1-hexene and 2.6 grams of 4methyl-1-pentene that had been cooled to 0°C. After four days, the resulting rigid reaction product was dissolved in 50 mL of toluene and poured into 200 mL of methanol to precipitate the product. After drying in a vacuum oven, the polymer weighed 23 grams. NMR analysis disclosed that the polymer contained 5 mole % 4-methyl-1-pentene. According to GPC analysis, the polymer had $M_w = 207,000$, $M_n = 62,000$ and PD 3.3.

Example 25

30 Preparation of high molecular weight polyhexene

A solution of 0.025 mmole $(fluorenyl)_2ZrMe_2$ (as described in Samuel et al. *J. Organomet. Chem.* 1976, 113, 331) in 0.5 mL of anhydrous toluene was added under N_2 to 0.025 mmole $(C_6F_5)_3B \cdot C_{11}H_9OH$ as prepared in Example 7 in 0.5 mL toluene. The resulting catalyst was added to 13.4 grams of 1-dry, oxygen-free 1-hexene at 0°C. The mixture was too thick to stir with a

- magnetic stirrer after 10 minutes. After approximately 16 hours, the reactor was opened to air and the contents dissolved in hot toluene. This solution was poured with stirring into a large excess of methanol.
- 5 After drying in a vacuum oven, the precipitated polymer weighed 9.2 grams. Low angle laser light scattering demonstrated that M_w was 2.15×10^6 . The polydispersity of the polymer was not obtainable because M_n was not independently known. However, polyhexenes were made
- 10 using the closely related $C_{10}H_7OB(C_6F_5)_2$, salts of (cyclopentadienyl)₂HfMe⁺ and (indenyl)₂HfMe⁺. The polymer polydispersities were 2.7 and 2.6 respectively. These are entries 8 and 10 shown in Table 1. Since polydispersity is essentially unaffected by
- 15 introduction of one fused benzene ring onto the cyclopentadienyl ligand it is believed the polyhexene prepared according to this and Example 26, wherein the ligand bound to the metal has two fused benzene rings, has a polydispersity of about three or less.

20

Example 26

High molecular weight polyhexene

- A reaction similar to that Example 25 was carried out using less catalyst such that the monomer:catalyst ratio was 37,700:1. Workup was accomplished by scraping the product from the reactor. From 40.2 grams of 1-hexene was obtained 9.8 grams of polymer. Light scattering analysis revealed that M_w was 3,390,000.

30

Example 27

Polymerization of 1-octadecene

- A solution in 0.5 mL toluene of the catalyst prepared as in Example 24 was added with stirring to 13.4 grams of 1-octadecene at 0°C. After approximately 35 16 hours, the crude product was slurried with warm isopropanol then dried at 160°C/40 Pa (0.3 mm Hg) to give 13.4 grams (85%) of a waxy polymer (m.p. 45°C).

GPC analysis indicated the polymers had a $M_w = 154,000$, $M_n = 72,000$ and PD = 2.14.

Example 28

5 Copolymerization of 1-hexene and 1,13-tetradecadiene

This example illustrates copolymerization of an olefin and a diolefin. A solution containing 0.025 mmole of the catalyst as prepared as Example 24 was added with stirring to a cold (0°C) mixture of 26.8 (319 mmol) of 1-hexene and 0.17 grams (0.88 mmol) of 1,13-C₁₄H₂₆, (Shell Co., Houston, TX). After approximately 16 hours at this temperature, the insoluble, tough, rubbery polymer was removed from the reactor, cut into small pieces, and then dried at 80°C under vacuum. The yield was 25.4 grams (94%).

A similar example was run but using instead 0.85 gram of the same diene. The yield of polymer, after vacuum drying, was 25.4 grams (92%).

20

Example 29

Polymerization of ethylene

In a nitrogen-filled drybox, a solution of 0.05 mmole of (indenyl)₂TiMe₂, as prepared according in 0.5 mL toluene was added to 0.05 mmole of C₆F₅B·C₁₄H₉OH in 0.5 mL of the same solvent. The flask was attached to a vacuum line, the contents frozen and the nitrogen pumped away. After thawing, ethylene was admitted until the pressure reached 80 kPa (600 mm Hg). The reactor was stirred and more ethylene was added so as to maintain the pressure at approximately 80 kPa during the exothermic polymerization. After ethylene consumption had declined, the now-solid reaction mixture was rinsed from the flask with methanol and air dried. The yield of polyethylene, identified by infrared spectroscopy, was 0.65 gram.

Example 30

Preparation of poly(cyclopentene)

This example illustrates the polymerization of a cyclo-olefin. To 14.7 grams of cyclopentene that had been cooled to 0°C was added a solution in 0.4 mL of 5 toluene of the catalyst as prepared in Example 24. The reactor was maintained at this temperature and shaken occasionally. After two days, the mixture was filtered. The solid phase, 1.4 grams, was digested with 50 mL of hot toluene to remove lower molecular weight oligomers and then filtered to provide 0.8 gram 10 of a white, insoluble solid. It was identified by infrared spectroscopy and X-ray powder diffraction as poly(cyclopentene).

Various modifications and alterations of this 15 invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth herein.

CLAIMS:

1. A borane complex comprising:
 - (a) tris(pentafluorophenyl)borane and
 - (b) at least one complexing compound
- 5 selected from the group comprising water, alcohol, mercaptan, silanols, and oximes.

2. The borane complex according to claim 1, having the general formula:

- 10 $(C_6F_5)_3B-(YXH)_q$,
wherein X is oxygen, or sulfur;
q is 1 to 3;
Y is a hydrogen atom, R^1- , $(R^2)_3Si-$, or
 $(R^3)_2C=N-$;
- 15 R^1 is a hydrocarbyl group containing 1 to 500 carbon atoms, and may contain a divalent oxygen and further may be a halogen-containing hydrocarbyl group;
- R^2 is independently a linear or branched alkyl
20 group containing 1 to 25 carbon atoms, or a phenyl group, further R^2 may contain a $SiO-$ group; and
- R^3 is independently a hydrocarbyl group containing 1 to 25 carbon atoms, R^3 may be a hydrogen
25 atom provided both R^3 groups selected are not hydrogen atoms.

3. The borane complex according to claim 1, wherein the R^1 group is $CH_3OC_2H_5-$, t-butylcyclohexyl,
30 isopropyl, allyl, benzyl, methyl, ethyl, $CF_3CF_2(C_2F_5)_nC_2H_5-$, where n has an average value of 3.5, $n-C_{11}H_{23}-$, or poly- α -olefin oligomer containing 2 to 100 olefin monomer units.

- 35 4. The borane complex according to claim 1, wherein Y is $(t-C_4H_9)((CH_3)_3Si-$ or $((CH_3)_2SiO)_2Si-$.

5. The borane complex according to claim 1,
wherein the borane complex is $(C_6F_5)_3B \cdot R^1OH$.

6. The borane complex according to claim 1,
5 wherein the borane complex is $(C_6F_5)_3B \cdot R^1SH$.

7. The borane complex according to claim 1,
wherein the borane complex is $(C_6F_5)_3B \cdot (R^2)_2SiOH$.

8. The borane complex according to claim 1,
10 wherein the borane complex is $(C_6F_5)_3B \cdot (R^3)_2C \cdot NOH$.

9. The borane complex according to claim 1,
wherein the borane complex is $(C_6F_5)_3B \cdot 3H_2O$.

15 10. The borane complex according to claim 1,
wherein the borane complex is $(C_6F_5)_3B \cdot H_2O$.

11. A catalyst comprising (a) a borane complex
and (b) a Group IVB organometallic compound.

20 12. The catalyst according to claim 1, wherein
the borane complex is neutral and has the general
formula $(C_6F_5)_3B \cdot (XYH)_q$ and the Group IVB organometallic
compound has the general formula $(Cp)_pM(R^4)_q$,
25 wherein M is titanium, zirconium or hafnium;

X is oxygen, or sulfur;

p is 1 or 2;

q is 1 to 3;

Y is a hydrogen atom, R^1- , $(R^2)_2Si-$, or $(R^3)_2C=N-$;

30 Cp is a cyclopentadienyl ligand, wherein each
carbon atom in the ligand may be,
independently, substituted with a radical
selected from the group consisting of
hydrocarbyl radicals, hydrocarbyl-substituted
35 metalloid radicals wherein the metalloid is
selected from Group IVA of the hydrocarbyl
and substituted-hydrocarbyl radicals contain

1 to 20 carbon atoms and further can include straight and branched alkyl groups, cyclic hydrocarbon groups, alkylsubstituted cyclic hydrocarbon groups, aromatic groups or alkyl-substituted aromatic groups; one or two pairs of adjacent hydrogen atoms of the cyclopentadienyl ligand may be substituted with one or two -(CH)_n groups to form indenyl or fluorenyl radicals, respectively, or compounds in which one or two methylene rings having the general formula (CH₂)_n, wherein n is 3 to 6 in the cyclopentadienyl ligand; further, when p is 2 the cyclopentadienyl ligand may be combined into one bidentate ligand molecule by connecting the cyclopentadienyl ligands by an organic or organometalloid group; and

R¹ is a hydrocarbyl group containing 1 to 500 carbon atoms, and may contain a divalent oxygen and further may be a halogen-containing hydrocarbyl group;

R² is independently a linear or branched alkyl group containing 1 to 25 carbon atoms, or a phenyl group, further R² may contain a SiO-group; and

R³ is independently a hydrocarbyl group containing 1 to 25 carbon atoms, R³ may be a hydrogen atom provided both R³ groups selected are not hydrogen atoms.

R⁴ is independently hydrogen or a hydrocarbyl or substituted hydrocarbyl group containing from 1 to 20 carbon atoms and may be a straight or branched alkyl group, and if sufficiently large enough, a cyclic hydrocarbyl group, an alkyl-substituted cyclohydrocarbyl group, an aromatic group, an aromatic-substituted alkyl group, or an alkylsubstituted aromatic group

and also include trisubstituted organometalloid groups of Group IVA elements wherein each hydrocarbyl group on the metalloid contains from 1 to 20 carbon atoms.

5

13. The catalyst according to claim 12, wherein Cp is a substituted or unsubstituted cyclopentadienyl, indenyl, or fluorenyl group.

10

14. The catalyst according to claim 12, wherein p is 2 and Cp is a cyclopentadienyl group.

15. The catalyst according to claim 12, wherein p is 2 and Cp is a indenyl group.

15

16. The catalyst according to claim 12, wherein p is 1 and Cp is a pentamethyl cyclopentadienyl group.

20

17. The catalyst according to claim 12, wherein p is 2 and Cp is fluorenyl group.

18. The catalyst according to claim 12, wherein XY is an oligomeric O-(poly- α -olefin) group.

25

19. The catalyst according to claim 12, wherein XY is OC₁₁H₂₃.

30

20. The catalyst according to claim 12, wherein XY is SC₁₁H₂₃.

35

21. The catalyst according to claim 11, wherein the borane complex is an acidic salt wherein the anion has the general formula (C₆F₅)₃B·XY and the Group IVB organometallic compound has the general formula (Cp)_pM(R⁴)_{4-p},

wherein M is titanium, zirconium or hafnium.

X is oxygen, or sulfur;

p is 1 or 2;
Y is a hydrogen atom, R¹-, (R²)₂Si-, or (R³)₂C=N-;
Cp is a cyclopentadienyl ligand, wherein each
carbon atom in the ligand may be,
5 independently, substituted with a radical
selected from the group consisting of
hydrocarbyl radicals, hydrocarbyl-substituted
metalloid radicals wherein the metalloid is
selected from Group IVA of the periodic table
10 of the elements, and wherein the hydrocarbyl
and substituted-hydrocarbyl radicals contain
1 to 20 carbon atoms and further can include
straight and branched alkyl groups, cyclic
hydrocarbon groups, alkylsubstituted cyclic
15 hydrocarbon groups, aromatic groups or alkyl-
substituted aromatic groups; one or two pairs
of adjacent hydrogen atoms of the
cyclopentadienyl ligand may be substituted
with one or two -(CH_n)₂ groups to form indenyl
20 or fluorenyl radicals, respectively, or
compounds in which one or two methylene rings
having the general formula (CH₂)_n, wherein n is
3 to 6 in the cyclopentadienyl ligand;
further, when p is 2 the cyclopentadienyl
25 ligand may be combined into one bidentate
ligand molecule by connecting the
cyclopentadienyl ligands by an organic or
organometalloid group; and
R¹ is a hydrocarbyl group containing 1 to 500
30 carbon atoms, and may contain a divalent
oxygen and further may be a halogen-
containing hydrocarbyl group;
R² is independently a linear or branched alkyl
group containing 1 to 25 carbon atoms, or a
35 phenyl group, further R² may contain a SiO-
group; and
R³ is independently a hydrocarbyl group containing

1 to 25 carbon atoms, R³ may be a hydrogen atom provided both R³ groups selected are not hydrogen atoms.

R⁴ is independently hydrogen or a hydrocarbyl or
5 substitutedhydrocarbyl group containing from 1 to 20 carbon atoms and may be a straight or branched alkyl group, and if sufficiently large enough, a cyclic hydrocarbyl group, an alkyl-substituted cyclohydrocarbyl group, an aromatic group, an aromatic-substituted alkyl group, or an alkylsubstituted aromatic group and also include trisubstituted 10 organometalloid groups of Group IVA elements wherein each hydrocarbyl group on the metalloid contains from 1 to 20 carbon atoms.
15

22. A method of polymerizing olefinically unsaturated monomers comprising:

- (a) contacting at a temperature range within 20 the range of about -90°C to about 300°C and at a pressure within the range of about 6.9 kPa to 310 MPa (1 to about 45,000 psig) monomers either alone or in combination with one or more monomers in a suitable carrier, solvent or diluent with a catalytically 25 effective amount of the catalyst according to claim 11, or claim 21.
(b) continuing the contacting of step (a) for a sufficient period of time to polymerize at least a portion of said monomers; and
30 (c) recovering a polymer product.

23. The method according to claim 22, wherein the olefinically unsaturated monomers have from 2 to 30 carbon atoms.

24. The method according to claim 23, wherein the olefinically unsaturated monomers have from 5 to 10 carbon atoms.

5 25. The method according to claim 22, wherein the olefinically unsaturated monomers are selected from the group consisting of linear- and branched α -olefins, cyclic olefins, olefins containing an aromatic group, olefins containing silicon and boron, diolefins and
10 mixtures thereof.

26. A polymer prepared according to claim 22, wherein the polymer has a weight average molecular weight of 100,000 to 5,000,000 and a polydispersity (PD) of molecular weights of less than or equal to 3.5.
15

27. A polymer prepared according to claim 25, wherein the starting olefinically unsaturated monomer is 1-hexene and the polymer has a weight average
20 molecular weight of 500,000 to 5,000,000 and a polydispersity of less than 3.5.

28. A polymer prepared according to claim 25, wherein the starting olefinically unsaturated monomer
25 is 1-octene and the polymer has a weight average molecular weight of 500,000 to 5,000,000 and a polydispersity of less than 3.5.

29. A polymer of a C_nH_{2n} monomer wherein $n \geq 5$ and
30 having weight average molecular weight of 100,000 to 5,000,000 and a polydispersity (PD) of molecular weights of less than or equal to 3.5.

30. A poly(1-hexene) polymer having a weight
35 average molecular weight of 500,000 to 5,000,000 and a polydispersity of less than 3.5.

31. A poly(1-octene) polymer having a weight average molecular weight of 500,000 to 5,000,000 and a polydispersity of less than 3.5.

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